A Model of CO_2 Absorption in Aqueous K_2CO_3/PZ

Jorge M. Plaza, Eric Chen, Gary Rochelle
Department of Chemical Engineering, The University of Texas at Austin

BACKGROUND

- A rate-based model for K_2CO_3 /PZ was developed using VLE by Hilliard (2005) and kinetics and speciation by Cullinane (2005)
- Cullinane used NTRL theory to predict VLE data and speciation for H_2O-K_2CO_3-PZ-CO_2. Equilibrium and interaction parameters regressed and rate constants and diffusion coefficients obtained
- Hilliard translated Cullinane into AspenPlus® using the electrolyte-NRTL model (2005).
- Chen carried out pilot plant campaigns for 5m/2.5m, 6.4m/1.6m K+/PZ.
- Heats of absorption inconsistencies were solved; heats of formation for PZ species and zwitterion considerations were included

OBJECTIVE

- Develop an optimization tool for the absorption of CO_2 in K_2CO_3 /PZ
- Analyze absorber optimization to minimize stripper reboiler duty and absorber height to meet 90% CO_2 removal with 4.5 m/ 4.5 m K+/PZ.
- Evaluate the effect of using semilean feed and intercooling in absorber.

RATESEP MODEL

Activity Based Constants

- Power law kinetics based on activities (not concentrations)
- Activity coefficients for 5m/ 2.5m, 4.5m/4.5 m K+/PZ By AspenPlus® Flash
- Ionic Strength correction since no option in AspenPlus®

$$r = k \cdot \left(\frac{T}{T_o}\right)^n \exp\left(\frac{-E}{R}\cdot\left(\frac{1}{T}-\frac{1}{T_o}\right)\right)\cdot\prod\left(x_i \cdot \gamma_i\right)^{\alpha_i}$$

Figure 1: Power law kinetics formula

- Hydroxide reactions not included in 2nd set. Concentration small when PZCOO- is present.
- Bicarbonate ion reactions included to properly model equilibrium in boundary layer and do not affect the CO_2 absorption rate.

Table 1: Activity based rate parameters for $PZ + CO_2 \xleftrightarrow{H_2O} PZCOO^- + H_3O^+$

Dir	5 m/2.5 m K+/PZ			4.5 m/4.5 m K+/PZ		
	k x 10^{12}	E (KJ/kmol)	n	k x 10^{12}	E (KJ/kmol)	n
Forward	2.00	-17,600	17.25	1.27	-42,400	23.48
Reverse	4.63	185,400	-33.04	2.93	160,600	-26.81

Effective Interfacial Area

- Literature correlations predicted inaccurate interfacial area.
- Data from NaOH experiments using 3 m of packing CMR-2 were regressed and results were included in the model.

$$PZ + CO_2 + \begin{cases} OH^- \xleftrightarrow{k_{PZ\text{-}OH^-}} PZCOO^- + H_2O \\ H_2O \xleftrightarrow{k_{PZ\text{-}H_2O}} PZCOO^- + H_3O \\ PZ \xleftrightarrow{k_{PZ\text{-}PZ}} PZCOO^- + PZH^+ \\ CO_3^{2-} \xleftrightarrow{k_{PZ\text{-}CO_3^{2-}}} PZCOO^- + HCO_3^- \\ PZCOO^- \xleftrightarrow{k_{PZ\text{-}PZCOO^-}} PZCOO^- + H^+PZCOO^- \end{cases}$$

$$PZCOO^- + CO_2 + \begin{cases} H_2O \xleftrightarrow{k_{PZCOO^- - H_2O}} PZ(COO^-)_2 + H_3O \\ PZ \xleftrightarrow{k_{PZCOO^- - PZ}} PZ(COO^-)_2 + PZH^+ \\ CO_3^{2-} \xleftrightarrow{k_{PZCOO^- - CO_3^{2-}}} PZ(COO^-)_2 + HCO_3^- \\ PZCOO^- \xleftrightarrow{k_{PZCOO^- - PZCOO^-}} PZ(COO^-)_2 + H^+PZCOO^- \end{cases}$$

Figure 2: PZ reactions included in the absorber model kinetics

$$CO_2 + OH^- \xleftrightarrow{k_{OH^-}} HCO_3^-$$
$$PZ + CO_2 + H_2O \xleftrightarrow{k_{PZ}} PZH^+ + HCO_3^-$$
$$PZCOO^- + CO_2 + H_2O \xleftrightarrow{k_{PZCOO^-}} H^+PZCOO^- + HCO_3^-$$

Figure 3: Bicarbonate reactions included in the absorber model

Physical Properties

- Aspen Plus® density values 5-10% below Cullinane. Regression work to be included in model
- Viscosity calculated from regressed model of Cullinane data.
- Default Aspen Plus® viscosity estimates were 70% lower.

RESULTS

Initial modeling case for 4.5m/4.5m K+/PZ

- Variable lean loadings (mol CO_2/alkalinity).

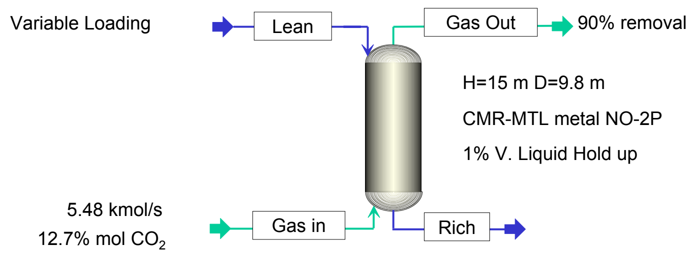

Figure 4: Initial modeling case conditions

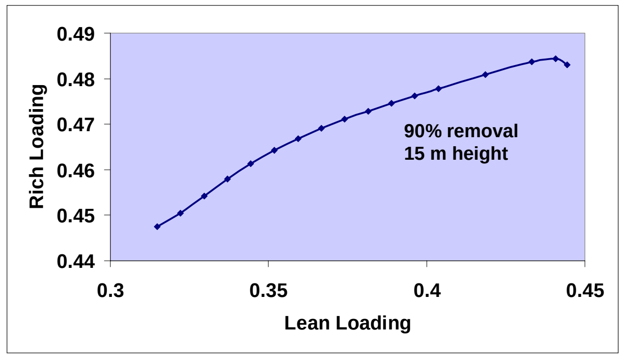

Figure 5: Absorber loading behavior 4.5/4.5 m PZ/K+

Optimization for 4.5m/4.5m K+/PZ

- Reduce stripper reboiler heat duty minimize absorber packing.
- Optimization based on CO_2 removal for a 500 MW plant

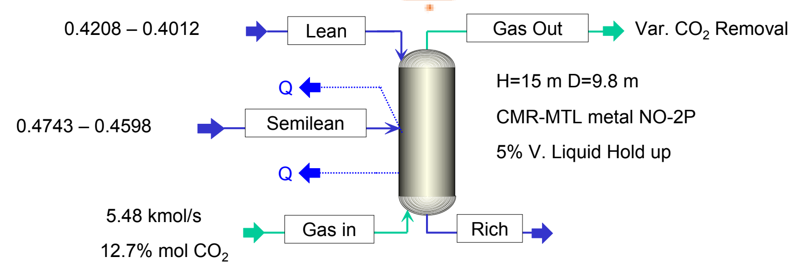

Figure 6: Optimization variables and configuration

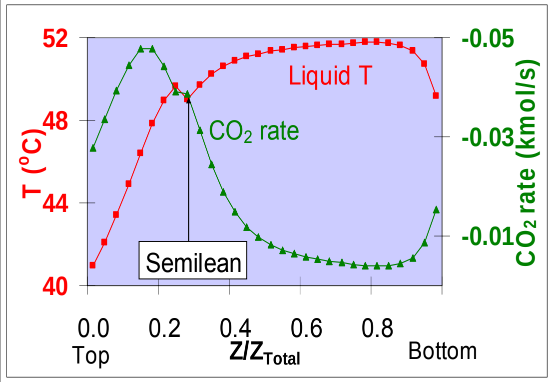

Figure 7: 0.4012 lean. No intercooling. 81.4% Removal

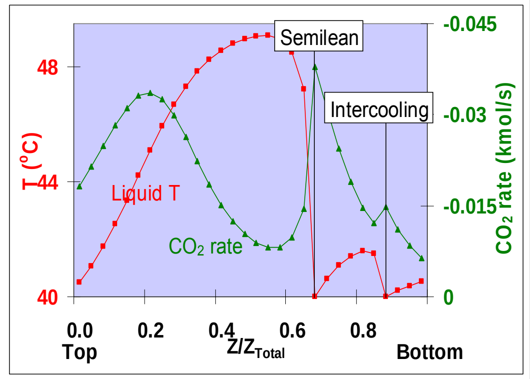

Figure 8: 0.4012 lean. Single intercooling. 88.3% Removal

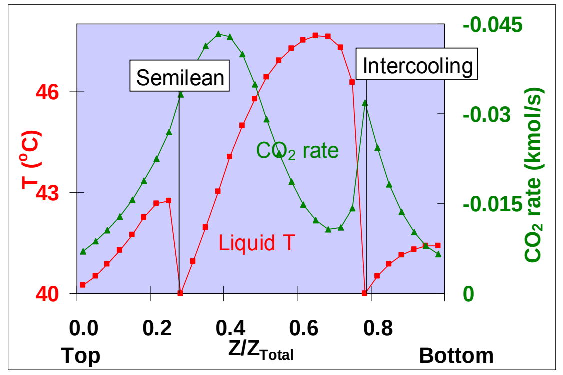

Figure 9 : 0.4012 lean. Double intercooling. 92.4% Removal

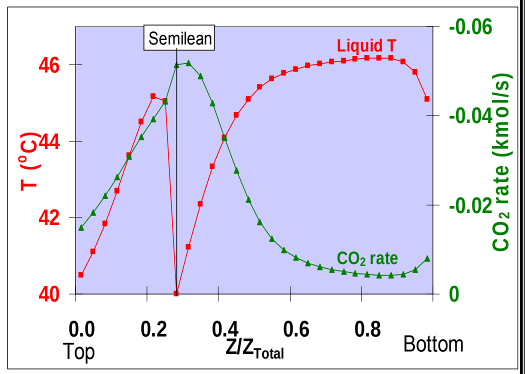

Figure 10: 0.4208 lean. Double intercooling 84.4% Removal

CO_2 P lean Solvent	0.5 kPa	0.7 kPa
Intercooling	**CO_2 Removal (%)**	
None	81.4	71.6
Single	88.3	82.9
Double	92.4	84.4

Table 2 : CO_2 removal results for the studied absorber configurations

CONCLUSIONS

- Without intercooling the absorber reaches a maximum T ≈52°C near the bottom.
- Intercooling improves absorber removal performance by more than 10% by reducing pinch points
- Double intercooling yields 92.4% removal with a loading of 0.40 lean and 0.46 semilean (5/0.5 kPa) for 4.5 m/4.5 m K+/PZ

ACKNOWLEDGEMENTS

- Aspen Technology provided the AspenPlus® software. This paper was prepared with the support of the TXU Carbon Management Program and of the U.S. Department of Energy, under Award No. DE-FC26-02NT41440[1]

[1]However, any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the DOE